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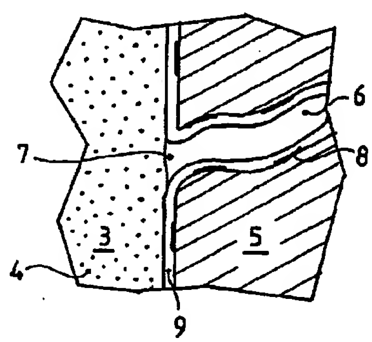
(54) Pile à combustible.

(57) La pile à combustible comprend au moins deux électrodes poreuses, un catalyseur (8) étant dispersé à la surface des pores (7). Les pores (7) et la face interne des électrodes sont revêtus d'un électrolyte solide sous forme d'un film (9) constitué d'un polymère à conduction protonique, et les électrodes enserrent par leur face interne une matrice (3) poreuse remplie d'un électrolyte liquide acide (4).

Le film solide (9) de polymère à conduction protonique, qui peut être un film continu, peut être constitué d'un aminosil du type:

$$(SiO_3)_2 - (CH_2)_3\ NH_2,\ HNX$$

ou un composé perfluoré.



FR 2 667 728 - A1

PILE A COMBUSTIBLE

La présente invention se rapporte à une pile à combustible, du type pile à combustible hydrogène-oxygène.

Depuis quelques années, on a atteint des performances très intéressantes dans les piles à combustible hydrogène-oxygène, dans lesquelles on emploie comme électrolyte une membrane en polymère à conduction protonique. Le système le plus efficace comporte des électrodes ayant une structure dite à triple contact, la liaison entre le catalyseur dispersé à la surface des pores de l'électrode et la membrane étant assurée par un film de polymère également conducteur protonique.

La demanderesse a mis en évidence que l'efficacité de la pile n'est pas liée à l'emploi d'une membrane comme électrolyte, mais essentiellement au mode de transport des espèces et des charges dans le domaine où coexistent catalyseur, film d'électrolyte solide et gaz. Il faut en effet noter que l'utilisation de membrane comporte divers inconvénients :

a) Pour des épaisseurs de membrane aisément réalisables industriellement, la résistance introduite par la membrane est supérieure, même pour les meilleurs matériaux dont on dispose actuellement, à celle induite par un électrolyte conventionnel d'épaisseur sensiblement équivalente.

b) Le maintien d'un bon équilibre d'hydratation de la membrane est un point délicat, le transport des molécules d'eau étant plus difficile au sein d'une membrane que dans un électrolyte liquide.

c) Le coût des membranes est actuellement un frein important au développement de ces piles.

En effet, bien qu'on puisse relever dans la littérature l'obtention de densités de courant pouvant atteindre 2 A/cm2, ce qui minimise la surface de membrane à utiliser (soit 0,1 m^2/kW), ces valeurs sont relatives à des électrodes comportant des taux de platinoïdes importants et sont obtenues pour des tensions de pile relativement faibles (0,5-0,6 V). Dans de nombreuses applications telles que dans les véhicules électriques, on devra opérer avec des rendements élevés et des électrodes dépourvues de platine, ce qui conduira à des densités de courant cinq à dix fois plus faibles. Dans ces conditions, même dans des hypothèses de grande production, l'utilisation de membrane conduirait à des surcoûts inadmissibles.

L'invention résoud ces problèmes en proposant une pile à combustible sans menbrane, laquelle comprend au moins deux électrodes poreuses, avantageusement du type à triple contact, un catalyseur étant dispersé à la surface des pores.

Les pores et la face interne des électrodes sont revêtus d'un film solide constitué d'un polymère à conduction protonique, et les électrodes enserrent par leur face interne une matrice poreuse remplie d'un électrolyte liquide acide.

Avantageusement, le film solide est continu et le diamètre des pores est choisi de telle façon que la tension capillaire assurant la rétention de l'électrolyte liquide dans la matrice est plus importante que celle qui existe entre l'électrolyte liquide et les pores constituant les électrodes. On est ainsi assuré d'une bonne cohésion et d'une bonne intégrité de structure.

De préférence, la résistance surfacique de la matrice imprégnée d'électrolyte liquide est inférieure à 0,3 Ohm.cm. La porosité de la matrice et son épaisseur sont choisies en conséquence.

L'électrolyte solide polymère peut être un aminosil du type $(SiO_3)_2$ - $(CH2)_3$ NH_2, NHX, un composé perfluoré, un polyphosphate ou une autre substance portant des charges ioniques ou apte à donner des H^+ libres.

Le film de conducteur protonique a avantageusement une épaisseur comprise entre 20 et 2 000 Angströms et la structure poreuse comprend au moins un constituant hydrophobe, par exemple du polytétrafluoroéthylène.

Les piles sans membrane selon l'invention ont des bonnes caractéristiques d'électrode et comportent dans leur structure un électrolyte polymère solide et un espace inter-électrode comportant un électrolyte liquide. On notera que le polymère incorporé à l'électrode à triple contact étant à conduction protonique, l'électrolyte liquide associé sera acide.

L'ensemble composite électrolyte liquide/électrode, considéré par exemple au niveau de la cathode ou s'opère la réduction de O_2, devra permettre de réaliser au mieux les fonctions suivantes :

a) le transfert électronique entre le catalyseur et le support de collecte de décharge,

b) le transfert aisé de O_2 de la phase gazeuse au catalyseur à travers un film d'électrolyte solide,

c) le transport aisé des protons jusqu'à l'interface réactionnelle,

d) l'élimination rapide des moles H_2O formées à l'interface réactionnelle vers la surface de l'électrode ou à la rigueur vers l'électrolyte liquide.

L'invention résulte d'un compromis. En effet, si la fonction (b) implique que la couche d'électrolyte solide recouvrant le catalyseur soit perméable à O_2 et la moins épaisse possible, la fonction (c), en revanche, recouvrant la caractéristique de conduction ionique de l'électrolyte s'effectuera d'autant mieux que l'épaisseur sera plus grande.

On a ainsi pu montrer qu'en fonction de la porosité de l'électrode, de l'aire de la surface réactionnelle et des densités locales de courant, cette épaisseur sera comprise entre 20 et 200 Angströms. Dans les cas où cette couche est discontinue et, si, comme cela est possible, elle est remplacée localement par un matériau hydrophobe et perméable à O_2, l'épaisseur de la couche de polymère peut être accrue jusqu'à une valeur de 2 000 Angströms.

La fonction (d) impose, dans le cas d'une élimination de H_2O à l'interface gaz/solide, une épaisseur la plus faible possible de cette couche. Par ailleurs la continuité de conduction ionique par H^+ entre les deux électrodes impose une jonction entre l'électrolyte liquide et l'électrolyte solide. Toutefois, il a été remarqué que dans le cas d'une électrolyte liquide libre, son confinement ne peut être limité à l'espace inter-électrode et par conséquent on observe un noyage des pores par l'électrolyte, ce qui dans ces conditions conduit à une polarisation excessive, car l'apport en O_2 se fait alors très mal. La matrice va donc avoir des pores très fins (par exemple inférieurs à 1 000 Angströms) mais en quantité telle que la conduction ionique de la matrice contenant son électrolyte soit convenable. Tel est le cas par exemple de structures poreuses en polypropylène ou polyéthylène où la porosité est obtenue par mélange du polymère avec une poudre fine de SiO_2. Les essais effectués montrent que le noyage est effectivement évité.

On peut préparer la pile à combustible très simplement en réalisant d'abord les électrodes par enduction ou laminage-compactage, les électrodes recevant une dispersion de catalyseurs par divers techniques, telles que réduction chimique, adsorption sélective, pulvérisation cathodique, etc. On presse alors deux électrodes, l'une pour O_2, l'autre pour H_2, sur la matrice poreuse qui a été préalablement imbibée d'électrolyte acide ou qui le sera après montage. Les électrodes diffèrent généralement, mais pas obligatoirement, par la nature du catalyseur selon qu'il s'agit de l'électrode à hydrogène ou de l'électrode à oxygène.

L'invention sera mieux comprise en référence aux dessins annexés, donnés à titre d'exemple non limitatif. Dans ces dessins, où toutes les vues sont en coupe :

- la figure 1 est une vue de principe, schématique, d'une pile à combustible selon l'invention,

- la figure 2 est une vue détaillée de l'interface entre le film solide et la matrice poreuse remplie d'électrolyte liquide, et

- la figure 3 est une vue agrandie de la figure 2, expliquant le fonctionnement de la pile.

Comme on le voit sur la figure 1 pour la clarté de laquelle on a représenté le film solide revêtant uniquement la face interne de l'électrode, la pile se compose de deux électrodes 1 et 2 enserrant une matrice poreuse 3 remplit d'un électrolyte liquide acide 4. Comme électrolyte liquide, on peut choisir par exemple l'acide sulfurique ou les acides phosphoriques. Quant à la matrice, qui bien sûr doit être isolante électriquement, elle peut être constituée de structures poreuses de polyéthylène ou de polypropylène mélangées avec une fine poudre de silice.

Comme on le voit plus en détail sur la figure 2, l'électrode est composée d'un substrat conducteur 5, qui peut être choisi parmi le carbone poreux, les carbures métalliques, etc. Le substrat 5 présente des pores 7 prolongés par des canaux 6, à la surface desquels a été dispersé un catalyseur 8. On trouve également du catalyseur sur la face interne de l'électrode, c'est-à-dire sur

la face de l'électrode en contact avec la matrice 3 poreuse chargée de l'électrolyte liquide 4.

Comme catalyseur 8, on peut utiliser le platine, les carbures métalliques, par exemple le carbure de tungstène pour l'électrode à hydrogène, ou encore des métaloporphyrines dispersées et pyrolysées pour l'électrode à oxygène. On trouve enfin, enrobant le tout, face interne de l'électrode et canaux 6, le film solide 9 constitué d'un polymère à conduction protonique. Comme polymère, on peut utiliser l'une des substances mentionnées plus haut, par exemple des polymères perfluorés portant des groupes SO_3^- tels que ceux vendus par Dow Chemical, ou par Du Pont de Nemours sous la marque Nafion.

Comme on le voit sur la figure 3, où c'est l'électrode à oxygène ou électrode positive qui a été représentée, le gaz oxygène vient en contact avec le catalyseur 8 en suivant un canal 6 et à travers le film 9. Sur ce catalyseur 8 arrive également des ions hydrogène en provenance de la matrice 3 remplie de l'électrolyte liquide 4 et les électrons fournis par le substrat conducteur 5. L'oxygène réagit avec ces entités pour former de l'eau, qui diffuse à travers le film solide 9 et est évacué par les canaux 6.

L'hydrogène peut être de l'hydrogène pur ou dilué dans des gaz inertes, N_2 ou CO_2 par exemple, ou encore un gaz de craquage d'ammoniac ou de reformage des alcools, gaz qui est riche en H_2.

L'oxygène peut être pur ou dilué par des gaz inerte, cas notamment de l'air.

Exemples 1 à 6

On réalise une électrode à triple contact par une opération d'empâtage par laminage-compactage dans une mousse métallique d'or (exemples 1 et 2) ou par enduction mécanique sur un substrat en carbone poreux par Stackpole sous la marque Stackpole PC 206 (exemples 3 et 4) ou par Zoltek sous la marque Panex PW3 (exemples 5 et 6), d'un mélange comportant 20 mg/cm² de noir de carbone vendu par Cabot sous la marque Vulcan (exemples 1, 3 et 5) ou par Degussa sous la marque Printex (exemples 2, 4 et 6), lequel est revêtu d'une dispersion de platine à raison de 10 % en masse par rapport au carbone, et d'un liant introduit sous la forme d'une suspension de polytétrafluoroéthylène PTFE 30 N telle que masse PTFE /(masse carbone + masse Pt) = 0,36 avant l'empâtage-séchage de la pâte et reprise par l'isopropanol pour le laminage, puis on sèche 2 h à 300°C. On imprègne sous vide cette électrode dans une solution de Nafion 117 (marque de De Pont de Nemours, distribué par Aldrich) à 5 % de telle façon que la masse de Nafion 117 soit comprise entre 5 et 10 mg/cm².

Après séchage, les deux électrodes ainsi constituées sont placées dans un montage qui les plaquent sur une matrice en polyéthylène poreux ayant une épaisseur de 0,2 mm, inbibée d' une solution 2N de H_2SO_4. En alimentant en O_2 l'une des électrodes et l'autre en H_2 avec une surpression d'environ 50 g/cm² on constate

qu'à 23°C le système débite sous une tension de 0,7 V un courant de l'ordre de 200 mA/cm^2, valeur sensiblement voisine pour tous les exemples 1 à 6.

REVENDICATIONS

1. Pile à combustible, comprenant au moins deux électrodes poreuses (1,2), un catalyseur (8) étant dispersé à la surface des pores (7), caractérisée en ce que les pores (7) et la face interne des électrodes (1,2) sont revêtus d'un électrolyte solide sous forme d'un film solide (9) constitué d'un polymère à conduction protonique, et que les électrodes (1,2) enserrent par leur face interne une matrice poreuse (3) remplie d'un électrolyte liquide acide (4).

2. Pile selon la revendication 1, caractérisée en ce que la tension capillaire assurant la rétention de l'électrolyte liquide dans la matrice (3) est supérieure à celle qui existe entre l'électrolyte liquide (4) et les pores (7) constituants les électrodes (1,2).

3. Pile selon la revendication 1 ou 2, caractérisée en ce que la résistance surfacique de la matrice (3) imprégnée d'électrolyte liquide (4) est inférieure à 0,3 Ohm.cm.

4. Pile selon la revendication 1, caractérisée en ce que le film solide (4) de polymère à conduction protonique est un film continu.

5. Pile selon la revendication 1, caractérisée en ce que l'électrolyte solide polymère est un aminosil du type :

$$(SiO_3)_2 - (CH_2)_3\ NH_2,\ HNX$$

6. Pile selon la revendication 1, caractérisée en ce que l'électrolyte solide polymère est un composé perfluoré.

7. Pile selon la revendication 1 ou 4, caractérisée en ce que le film (4) de conducteur protonique a une épaisseur comprise entre 20 et 2 000 Angströms.

8. Pile selon la revendication 1, caractérisée en ce que le substrat poreux (5) dans lequel est dispersé le catalyseur (8) et sur lequel est déposé le film (7) de conducteur protonique, comprend au moins un constituant hydrophobe.

9. Pile selon la revendication 8, caractérisée en ce que le constituant hydrophobe est du polytétrafluoroéthylène.

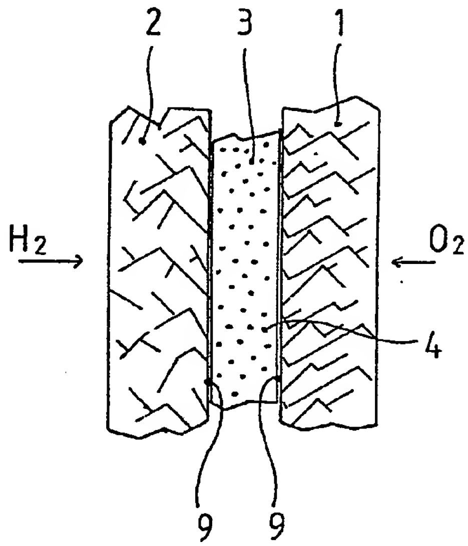


FIG 1

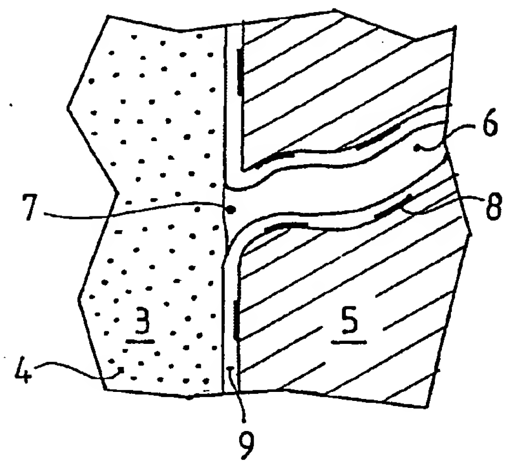


FIG 2

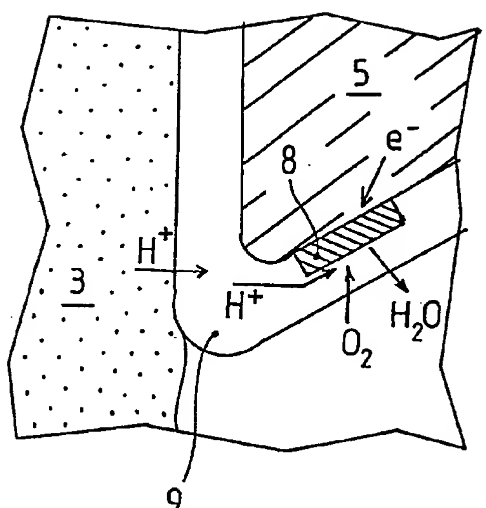


FIG 3

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RAPPORT DE RECHERCHE

établi sur la base des dernières revendications déposées avant le commencement de la recherche

FR 9012583
FA 450805

DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes	Revendications concernées de la demande examinée
X	EXTENDED ABSTRACTS, vol. 86-1, 4-9 mai 1986, abrégé no. 537, Spring Meeting, Boston, MA, US; S. SRINIVASAN et al.: "Enhanced electrode kinetics in phosphoric acid fuel cells by use of nafion coated porous gas diffusion electrodes" * Page 773, colonne de gauche, paragraphes 2-3; colonne de droite, paragraphe 2 * ---	1,4,6
Y	IDEM ---	2,8,9
Y	US-A-4 610 938 (A.J. APPLEBY) * Revendications 1,4; colonne 1, lignes 56-61; colonne 2, ligne 34 - colonne 3, ligne 20; exemple * ---	8,9
Y	GB-A-2 047 457 (ENERGY RESEARCH CORP.) * Revendication 18 * ---	2
Y	CH-A- 510 332 (AG BROWN & BOVERI) * Colonne 3, lignes 56-58; revendication 1 * ---	2
X	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 75 (E-306)[1798], 4 avril 1985; & JP-A-59 209 278 (HITACHI SEISAKUSHO K.K.) 27-11-1984 * Abrégé entier * ---	1,4,6
Y	US-A-4 517 260 (K. MITSUDA) * Revendication 1; figure 2a; colonne 4, lignes 3-10 * --- -/-	1

DOMAINES TECHNIQUES RECHERCHES (Int. Cl.5)

H 01 M

Date d'achèvement de la recherche	Examinateur
25-06-1991	D'HONDT J.W.

CATEGORIE DES DOCUMENTS CITES

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DOCUMENTS CONSIDERES COMME PERTINENTS		Revendications concernées de la demande examinée	
Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes		
Y	US-A-3 276 910 (R. GRASSELLI et al.) * Revendications 1,2; colonne 5, lignes 28-35 *	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 239 (E-206)[1384], 25 octobre 1983; & JP-A-58 128 668 (HITACHI SEISAKUSHO) 01-08-1983 * Abrégé en entier *	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 187 (E-516)[2634], 16 juin 1987; & JP-A-62 017 953 (HITACHI LTD) 26-01-1987 * Abrégé en entier *	1	
A	EXTENDED ABSTRACTS, vol. 86-2, 19-24 octobre 1986, abrégé no. 160, page 237, Princeton, NJ, US; M.N. SZENTIMAY et al.: "Oxygen reduction at perfluorosulfonate ionomer film-coated Pt electrodes - Kinetics and permeability" * Page 237, colonne de gauche, paragraphe 2 *	1	DOMAINES TECHNIQUES RECHERCHES (Int. Cl.5)
A	US-A-3 297 484 (L.W. NIEDRACH) * Revendications 1,11,12 *	1	

Date d'achèvement de la recherche	Examinateur
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References Cited:	Indicated at the end of this document.

FUEL CELL

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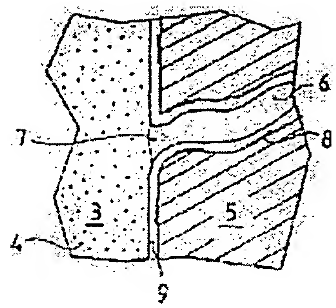
[Abstract]

The fuel cell comprises at least two porous electrodes, a catalyst (8) being dispersed on the surface of the pores (7). The pores (7) and the inner face of the electrodes are lined with a solid electrolyte in the form of a film (9) consisting of a proton-conducting polymer, and the electrodes enclose, by their internal face, a porous matrix (3) filled with an acidic liquid electrolyte (4).

The solid film (9) of proton-conducting polymer, which may be a continuous film, may consist of an aminosil of the type:

$$(SiO_3)_2 - (CH_2)_3\ NH_2,\ HNX$$

or a perfluorinated compound.



The invention concerns a fuel cell of the hydrogen-oxygen type.

For several years now, attempts have been made to achieve very interesting performances in hydrogen-oxygen fuel cells, in which a proton-conducting polymer membrane is used as the electrolyte. The most effective system involves the use of electrodes having a so-called triple contact structure, with a polymer film that also conducts protons acting as the link between the catalyst dispersed over the surface of the pores of the electrode and the membrane.

The applicant has shown that the effectiveness of the cell is not linked to the use of a membrane as the electrode, but in essence to the mode of conveying the forms and charges in the field where the catalyst, the solid electrode film, and the gas coexist. In fact, it should be noted that the use of a membrane involves a number of disadvantages:

a) For membrane thicknesses that are easily produced industrially, the resistance introduced by the membrane is greater, even for the best currently available materials, than that produced by a conventional electrolyte with roughly the same thickness.

b) Maintaining good hydration balance in the membrane is quite delicate, since the conveyance of water molecules is more difficult in a membrane than in a liquid electrolyte.

c) The cost of membranes is currently a significant obstacle to the development of such cells.

In fact, while the literature does report that current densities may be as high as 2 A/cm^2, which minimizes the membrane surface to be used (namely, 0.1 m^2/kW), these values are relative to electrodes that have significantly high platinoid levels and are obtained in relatively low voltage cells (0.5-0.6 V). In many applications, such as electric vehicles, it is necessary to operate with high efficiencies and with platinum-free electrodes, which results in current densities that are five to ten times lower. In these conditions, even if mass produced, the use of a membrane would lead to unacceptable additional cost.

The invention solves these problems by offering a fuel cell without membrane, which comprises at least two porous electrodes, advantageously of the triple contact type, with a catalyst dispersed over the surface of the pores.

The pores and the inner face of the electrodes are lined with a solid film consisting of a proton-conducting polymer, and the electrodes enclose by their internal face a porous matrix filled with an acidic liquid electrolyte.

Advantageously, the solid film is continuous, and the diameter of the pores is chosen so that the capillary tension that holds the liquid electrolyte in the matrix is greater than that between the liquid electrolyte and the pores that form the electrodes. This guarantees good cohesion and good structural integrity.

The surface resistance of the matrix filled with liquid electrolyte is preferably less than 0.3 $\Omega \cdot cm$. The porosity of the matrix and its thickness are chosen accordingly.

The solid polymer electrolyte may be an aminosil of the type $(SiO_3)_2$-$(CH_2)_3$ NH_2, HNX, a perfluorinated compound, a polyphosphate, or substance carrying ionic charges or capable of producing free H^+.

The thickness of the proton-conducting film is advantageously between 20 and 2000 Å, and the porous structure comprises at least one hydrophobic ingredient, such as a polytetrafluoroethylene.

The cells without membrane according to the invention have good electrode characteristics and contain in their structure a solid polymer electrolyte and an interelectrode space containing a liquid electrolyte. It should be noted that because the polymer incorporated in the triple-contact electrode is proton conducting, the related liquid electrolyte shall be acidic.

The liquid electrolyte/electrode compound unit, when considered for example from the standpoint of the cathode where O_2 reduction takes place, should be capable of performing at best the following functions:

a) electronic transfer between the catalyst and the discharge collecting support;

b) easy O_2 transfer from the gaseous phase to the catalyst through a solid electrolyte film;

c) easy proton transfer to the reaction interface;

d) speedy elimination of the H_2O moles formed at the reaction interface towards the surface of the electrode or if need be towards the liquid electrolyte.

The invention results in a compromise. In fact, if function (b) implies that the solid electrolyte layer coating the catalyst is permeable to O_2 and is as thin as possible, function (c), on the other hand, as regards the ionic conduction characteristics of the electrolyte, would work better if it were thicker.

Thus, it has been possible to show that in function of the porosity of the electrode, reaction surface area, and local current densities, this thickness shall be comprised between 20

and 200 Å. In the case where the layer is discontinuous and if possible locally replaced by a hydrophobic material that is permeable to O_2, the thickness of the polymer layer may be increased up to a value of 2000 Å.

In the case of H_2O elimination to the gas/solid interface, function (d) requires that this layer be as thin as possible. What is more, the continuity of ionic conduction by H^+ between the two electrodes requires a connection between the liquid electrolyte and the solid electrolyte. However, it has been noted that in the case of a free liquid electrolyte, its containment cannot be confined to the interelectrode space, and as a result flooding of the pores by the electrolyte has been known to happen, which under these conditions would result in excessive polarization since the O_2 intake would function very poorly. Therefore, the matrix will have very small pores (less than 1000 Å, for example), but of sufficient quantity to ensure good ionic conduction of the matrix containing the electrolyte. This is the case, for example, of porous structures of polypropylene or polyethylene where porosity is obtained by mixing the polymer with a fine SiO_2 powder. Tests have shown that flooding is effectively prevented.

The fuel cell may be very simply manufactured by first making the electrodes by coating or laminating-compacting them, with the electrodes receiving catalyser dispersion by means of a variety of methods, such as chemical reduction, selective adsorption, cathode pulverization, etc. Then, the two electrodes, one for O_2 and the other for H_2, are pressed onto the porous matrix that has already been saturated with acidic electrolyte or which will be after assembly. The electrodes differ generally, although not necessarily, in the nature of the catalyst depending on whether it is a hydrogen or an oxygen electrode.

The invention will be better understood with reference to the attached drawings, given by way of nonlimiting example. In these drawings, which are all cross sections:

- Figure 1 is a schematic view showing the principle of the fuel cell according to the invention;

- Figure 2 is a detailed view of the interface between the solid film and the porous matrix filled with liquid electrolyte; and

- Figure 3 is an enlarged view of Figure 2, explaining how the cell works.

As Figure 1 shows, where for reasons of clarity the solid film is shown coating the internal face only of the electrode, the cell consists of two electrodes 1 and 2 enclosing porous matrix 3 filled with acidic liquid electrolyte 4. For the liquid electrolyte, it is possible to choose sulfuric acid or phosphoric acids, for example. As far as the matrix is concerned, which must certainly be electrically insulating, it may be made of porous structures of polyethylene or polypropylene mixed with a fine silica powder.

As Figure 2 shows in greater detail, the electrode is composed of conducting substrate 5, which may be chosen from among porous carbons, metal carbides, etc. Substrate 5 has pores 7

extended by channels 6, on the surface of which catalyst 8 is dispersed. Catalyst is also to be found on the internal face of the electrode, in other words, on the face of the electrode that is in contact with porous matrix 3 filled with liquid electrolyte 4.

For catalyst 8, it is possible to use platinum, metal carbides, such as tungsten carbide, for example, for the hydrogen electrode, or dispersed and pyrolyzed metal porphyrins for the oxygen electrode. Finally, coating the whole thing, the internal face of the electrode and channels 6, is solid film 9 consisting of a proton-conducting polymer. For the polymer, it is possible to use one of the above-mentioned substances, such as perfluorinated polymers carrying SO_3- groups such as those sold by Dow Chemical, or by Du Pont de Nemours under the Nafion trademark.

As Figure 3 shows, where the oxygen or positive electrode is illustrated, oxygen gas comes into contact with catalyst 8 by taking channel 6 and passing through film 9. Also arriving at catalyst 8 are hydrogen ions from matrix 3 filled with liquid electrolyte 4 and the electrons supplied by conducting substrate 5. The oxygen reacts with these entities to form water, which is diffused through solid film 9 and eliminated via channels 6.

The hydrogen may be pure or diluted with inert gases, such as N_2 or CO_2, for example., or even an ammonium cracking or alcohol reforming gas, which is rich in H_2. The oxygen may be pure or diluted with inert gases, such as air in particular.

Examples 1 to 6

A triple contact electrode is made by means of a coating operation by laminating-compacting in a gold metallic foam (Examples 1 and 2), or by mechanically coating a substrate of porous carbon made by Stackpole under the brand name Stackpole PC 206 (Examples 3 and 4), or by Zoltek under the brand name Panex PW3 (Examples 5 and 6) with a mixture containing 20 mg/cm^2 of carbon black sold by Cabot under the brand name Vulcan (Examples 1, 3, and 5) or by Degussa under the brand name Printex (Examples 2, 4, and 6), which is lined with a platinum dispersion at a rate of 10 wt% in relation to the carbon, and a binder in the form of a suspension of polytetrafluoroethylene PTFE 30 N, such that the PTFE weight / (carbon weight + Pt weight) = 0.36 before coating-drying the mixture and reworking it with isopropanol for lamination, and then it is dried for 2 h at 300°C. This electrode is vacuum-filled with a solution of Nafion 117 (Du Pont de Nemours trademark distributed by Aldrich) at 5%, so that the weight of the Nafion 117 is between 5 and 10 mg/cm^2.

After drying, the two electrodes so formed are placed in an assembly that plates them onto a matrix of porous polyethylene with a thickness of 0.2 mm, saturated with a 2N solution of H_2SO_4. By supplying one of the electrodes with O_2 and the other with H_2, with suppression of about 50 g/cm^2, we find that at 23°C the system yields current on the order of 200 mA/cm^2 at a voltage of 0.7 V, which value is roughly the same for all Examples 1 to 6.

Claims

1. Fuel cell comprising at least two porous electrodes (1, 2), a catalyst (8) being dispersed on the surface of the pores (7), characterized in that the pores (7) and the inner face of the electrodes (1, 2) are lined with a solid electrolyte in the form of a solid film (9) consisting of a proton-conducting polymer, and that the electrodes (1, 2) enclose, by their internal face, a porous matrix (3) filled with an acidic liquid electrolyte (4).

2. Cell according to Claim 1, characterized in that the capillary tension that holds the liquid electrolyte in the matrix (3) is greater than that between the liquid electrolyte (4) and the pores (7) that constitute the electrodes (1, 2).

3. Cell according to Claim 1 or 2, characterized in that the surface resistance of the matrix (3) filled with liquid electrolyte (4) is less than 0.3 Ω·cm.

4. Cell according to Claim 1, characterized in that the solid film (4) [sic] of the proton-conducting polymer is a continuous film.

5. Cell according to Claim 1, characterized in that the solid polymer film is an aminosil of the type:

$$(SiO_3)_2 - (CH_2)_3\ NH_2,\ HNX.$$

6. Cell according to Claim 1, characterized in that the solid polymer electrolyte is a perfluorinated compound.

7. Cell according to Claim 1 or 4, characterized in that the thickness of the proton-conducting film (4) [sic] is between 20 and 2000 Å.

8. Cell according to Claim 1, characterized in that the porous substrate (5) on which the catalyst (8) is dispersed and on which the proton-conducting film (7) [sic] is deposited, contains at least one hydrophobic ingredient.

9. Cell according to Claim 8, characterized in that the hydrophobic ingredient is a polytetrafluoroethylene.

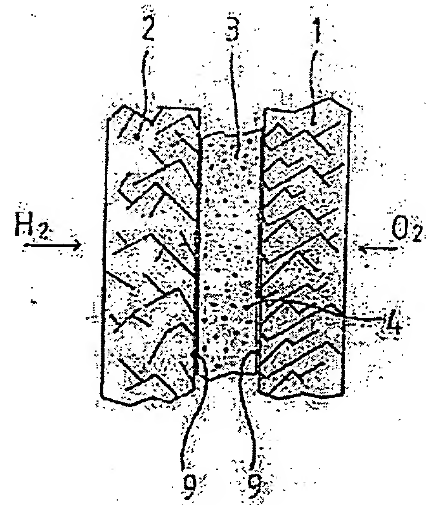


FIG 1

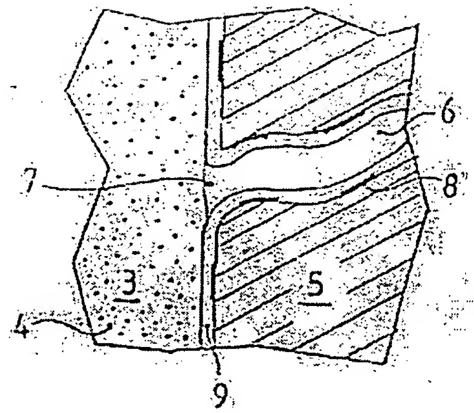


FIG 2

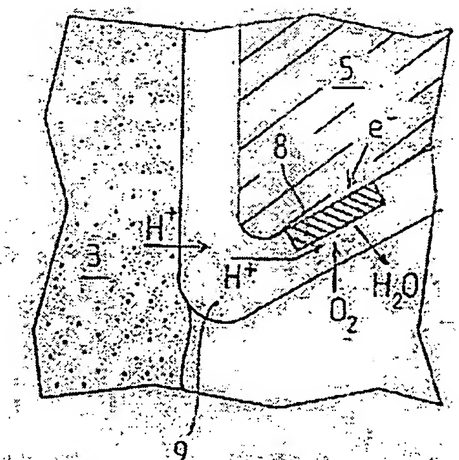


FIG 3

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SEARCH REPORT
established on the basis of the most recent claims filed before the start of the search

Fr 9012583
FA 450805

DOCUMENTS CONSIDERED TO BE RELEVANT		Claims concerned in the examined document	
Category	Citation of document with indication where appropriate, of relevant passages		
Y	US-A-3 276 910 (R. GRASSELLI et al.) *Claims 1, 2; column 5, lines 28-35* ---	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 7, No. 239 (E-206) [1384], October 25, 1983; & JP-A-58 128 668 (HITACHI SEISAKUSHO) August 1, 1983 *entire abstract* ---	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 11, No. 187 (E-516) [2634], June 16, 1987; & JP-A-62 017 953 (HITACHI LTD) January 26, 1987 *entire abstract* ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.^{5})
A	EXTENDED ABSTRACTS, vol. 86-2, October 19-24, 1986, abstract No. 160, page 237, Princeton, NJ, US: M.N. SZENTIMAY et al.: "Oxygen Reduction at Perfluorosulfonate Ionomer Film-coated Pt Electrodes - Kinetics and Permeability" *Page 237, left column, paragraph 2* ---	1	
A	US-A-3 297 484 (L.W. NIEDRACH) *Claims 1, 11, 12* ----	1	

Date of completion of the search	Examiner
June 25, 1991	J. W. D'Hondt

CATEGORY OF CITED DOCUMENTS

X: Particularly relevant if taken alone.
Y: Particularly relevant if combined with another document of the same category.
A: Technological background.
O: Non-written disclosure.
P: Intermediate document.
T: Theory or principle underlying the invention.
E: Earlier patent document, but published on, or after the filing date.
D: Document cited in the application.
L: Document cited for other reasons.

&: Member of the same patent family, corresponding document.

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Category	DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document with indication where appropriate, of relevant passages	Claims concerned in the examined document	
X	EXTENDED ABSTRACTS, vol. 86-1, May 4-9, 1986, abstract No. 537, Spring Meeting, Boston, MA, US; S. SRINIVASAN et al.: "Enhanced Electrode Kinetics in Phosphoric Acid Fuel Cells by Use of Nafion Coated Porous Gas Diffusion Electrodes" *Page 773, left column, paragraphs 2-3; right column, paragraph 2*	1,4,6	
Y	--- IDEM	2,8,9	
Y	--- US-A-4 610 938 (A.J. APPLEBY) *Claims 1, 4; column 1, lines 56-61; column 2, line 34 – column 3, line 20; example*	8,9	
Y	--- GB-A-2 047 457 (ENERGY RESEARCH CORP.) *Claim 18*	2	TECHNICAL FIELDS SEARCHED (Int. Cl.^{5})
Y	--- CH-A-510 332 (AG BROWN & BOVERI) *column 3, lines 56-58; Claim 1*	2	H 01 M
X	--- PATENT ABSTRACTS OF JAPAN, vol. 9, No. 75 (E-306) [1798] April 4, 1985; & JP-A-59 209 278 (HITACHI SEISAKUSHO K.K.) November 27, 1984 *entire abstract*	1,4,6	
Y	--- US-A-4 517 260 (K. MITSUDA) *Claim 1; Figure 2a; column 4, lines 3-10* --- -/-	1	

Date of completion of the search	Examiner
June 25, 1991	J. W. D'Hondt

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D: Document cited in the application.
L: Document cited for other reasons.

&: Member of the same patent family, corresponding document.

DERWENT-ACC-NO: 1992-177254
DERWENT-WEEK: 199222

TITLE: Hydrogen-oxygen fuel cell - uses solid electrolyte made of conductive polymer over porous electrodes which enclose porous matrix holding acid electrolyte

INVENTOR: BESSE, S; BRONOEL, G ; TASSIN, N

PATENT-ASSIGNEE: SORAPEC SARL [SORAN]

PRIORITY-DATA: 1990FR-0012583 (October 8, 1990)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
FR 2667728 A1	April 10, 1992	N/A	015	H01M 004/86

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
FR 2667728A1	N/A	1990FR-0012583	October 8, 1990

INT-CL (IPC): H01M004/86; H01M008/00
ABSTRACTED-PUB-NO: FR 2667728A

BASIC-ABSTRACT:
The fuel cell has two porous electrodes (1,2) with a catalyser (8) dispersed over the pores (7). The pores and the internal face of the electrodes are coated with a solid electrolyte formed as a solid film (9) of a conductive polymer. The electrodes enclose a porous matrix (3) filled with an acidic liq. electrolyte (4).

The capillary tension that retains liq. electrolyte in the matrix is greater than that between the liq. electrolyte and the electrode pores.

ADVANTAGE - Fuel cell without membrane, reducing cost of mfr. and reducing cell internal resistance.

CHOSEN-DRAWING: Dwg.2/3

W00054351(A1).pdf

CLIPPEDIMAGE= FR002667728A1
PUB-NO: FR002667728A1
DOCUMENT-IDENTIFIER: FR 2667728 A1
TITLE: Fuel cell

PUBN-DATE: April 10, 1992

INVENTOR-INFORMATION:

NAME	COUNTRY
GUY, BRONOEL	N/A
SERGE, BESSE	N/A
NOELLE, TASSIN	N/A

ASSIGNEE-INFORMATION:

NAME	COUNTRY
SORAPEC	FR

APPL-NO: FR09012583
APPL-DATE: October 8, 1990

PRIORITY-DATA: FR09012583A (October 8, 1990)
INT-CL_(IPC): H01M004/86; H01M008/00
EUR-CL (EPC): H01M004/86; H01M008/08

ABSTRACT:
The fuel cell comprises at least two porous electrodes, a catalyst (8) being dispersed on the surface of the pores (7). The pores (7) and the inner face of the electrodes are lined with a solid electrolyte in the form of a film (9) consisting of a proton conduction polymer, and the electrodes enclose, by their internal face, a porous matrix (3) filled with an acidic liquid electrolyte (4).

The solid film (9) of proton conduction polymer, which may be a continuous film, may consist of an aminosil of the type: <IMAGE> or a perfluorinated compound. <IMAGE>

French Patent No. 2 667 728 A1

Job No.: 6310-89224 Ref.: FR 2667728
Translated from French by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

FRENCH REPUBLIC
NATIONAL INSTITUTE OF INDUSTRIAL PROPERTY
PATENT NO. 2 667 728 A1

Int. Cl.[illegible]: H 01 M 4/86
8/00

Filing No.: 90 12583

Filing Date: October 8, 1990

Publication Date: April 10, 1992
Bulletin 92/15

References Cited: Indicated at the end of this document.

FUEL CELL

Inventors: Guy Bronoel, Serge Besse, and Noëlle Tassin

Applicant: Sorapec Société Anonyme - FR.

Agent: Cabinet Michel Moinas.

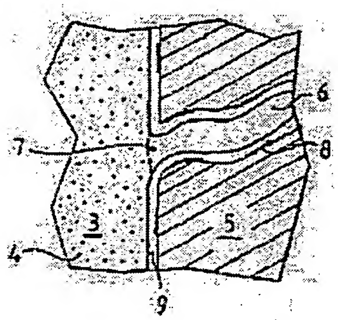
[Abstract]

The fuel cell comprises at least two porous electrodes, a catalyst (8) being dispersed on the surface of the pores (7). The pores (7) and the inner face of the electrodes are lined with a solid electrolyte in the form of a film (9) consisting of a proton-conducting polymer, and the electrodes enclose, by their internal face, a porous matrix (3) filled with an acidic liquid electrolyte (4).

The solid film (9) of proton-conducting polymer, which may be a continuous film, may consist of an aminosil of the type:

$$(SiO_3)_2 - (CH_2)_3\ NH_2,\ HNX$$

or a perfluorinated compound.



The invention concerns a fuel cell of the hydrogen-oxygen type.

For several years now, attempts have been made to achieve very interesting performances in hydrogen-oxygen fuel cells, in which a proton-conducting polymer membrane is used as the electrolyte. The most effective system involves the use of electrodes having a so-called triple contact structure, with a polymer film that also conducts protons acting as the link between the catalyst dispersed over the surface of the pores of the electrode and the membrane.

The applicant has shown that the effectiveness of the cell is not linked to the use of a membrane as the electrode, but in essence to the mode of conveying the forms and charges in the field where the catalyst, the solid electrode film, and the gas coexist. In fact, it should be noted that the use of a membrane involves a number of disadvantages:

a) For membrane thicknesses that are easily produced industrially, the resistance introduced by the membrane is greater, even for the best currently available materials, than that produced by a conventional electrolyte with roughly the same thickness.

b) Maintaining good hydration balance in the membrane is quite delicate, since the conveyance of water molecules is more difficult in a membrane than in a liquid electrolyte.

c) The cost of membranes is currently a significant obstacle to the development of such cells.

In fact, while the literature does report that current densities may be as high as 2 A/cm^2, which minimizes the membrane surface to be used (namely, 0.1 m^2/kW), these values are relative to electrodes that have significantly high platinoid levels and are obtained in relatively low voltage cells (0.5-0.6 V). In many applications, such as electric vehicles, it is necessary to operate with high efficiencies and with platinum-free electrodes, which results in current densities that are five to ten times lower. In these conditions, even if mass produced, the use of a membrane would lead to unacceptable additional cost.

The invention solves these problems by offering a fuel cell without membrane, which comprises at least two porous electrodes, advantageously of the triple contact type, with a catalyst dispersed over the surface of the pores.

The pores and the inner face of the electrodes are lined with a solid film consisting of a proton-conducting polymer, and the electrodes enclose by their internal face a porous matrix filled with an acidic liquid electrolyte.

Advantageously, the solid film is continuous, and the diameter of the pores is chosen so that the capillary tension that holds the liquid electrolyte in the matrix is greater than that between the liquid electrolyte and the pores that form the electrodes. This guarantees good cohesion and good structural integrity.

The surface resistance of the matrix filled with liquid electrolyte is preferably less than 0.3 $\Omega \cdot cm$. The porosity of the matrix and its thickness are chosen accordingly.

The solid polymer electrolyte may be an aminosil of the type $(SiO_3)_2$-$(CH_2)_3$ NH_2, HNX, a perfluorinated compound, a polyphosphate, or substance carrying ionic charges or capable of producing free H^+.

The thickness of the proton-conducting film is advantageously between 20 and 2000 Å, and the porous structure comprises at least one hydrophobic ingredient, such as a polytetrafluoroethylene.

The cells without membrane according to the invention have good electrode characteristics and contain in their structure a solid polymer electrolyte and an interelectrode space containing a liquid electrolyte. It should be noted that because the polymer incorporated in the triple-contact electrode is proton conducting, the related liquid electrolyte shall be acidic.

The liquid electrolyte/electrode compound unit, when considered for example from the standpoint of the cathode where O_2 reduction takes place, should be capable of performing at best the following functions:

a) electronic transfer between the catalyst and the discharge collecting support;

b) easy O_2 transfer from the gaseous phase to the catalyst through a solid electrolyte film;

c) easy proton transfer to the reaction interface;

d) speedy elimination of the H_2O moles formed at the reaction interface towards the surface of the electrode or if need be towards the liquid electrolyte.

The invention results in a compromise. In fact, if function (b) implies that the solid electrolyte layer coating the catalyst is permeable to O_2 and is as thin as possible, function (c), on the other hand, as regards the ionic conduction characteristics of the electrolyte, would work better if it were thicker.

Thus, it has been possible to show that in function of the porosity of the electrode, reaction surface area, and local current densities, this thickness shall be comprised between 20

and 200 Å. In the case where the layer is discontinuous and if possible locally replaced by a hydrophobic material that is permeable to O_2, the thickness of the polymer layer may be increased up to a value of 2000 Å.

In the case of H_2O elimination to the gas/solid interface, function (d) requires that this layer be as thin as possible. What is more, the continuity of ionic conduction by H^+ between the two electrodes requires a connection between the liquid electrolyte and the solid electrolyte. However, it has been noted that in the case of a free liquid electrolyte, its containment cannot be confined to the interelectrode space, and as a result flooding of the pores by the electrolyte has been known to happen, which under these conditions would result in excessive polarization since the O_2 intake would function very poorly. Therefore, the matrix will have very small pores (less than 1000 Å, for example), but of sufficient quantity to ensure good ionic conduction of the matrix containing the electrolyte. This is the case, for example, of porous structures of polypropylene or polyethylene where porosity is obtained by mixing the polymer with a fine SiO_2 powder. Tests have shown that flooding is effectively prevented.

The fuel cell may be very simply manufactured by first making the electrodes by coating or laminating-compacting them, with the electrodes receiving catalyser dispersion by means of a variety of methods, such as chemical reduction, selective adsorption, cathode pulverization, etc. Then, the two electrodes, one for O_2 and the other for H_2, are pressed onto the porous matrix that has already been saturated with acidic electrolyte or which will be after assembly. The electrodes differ generally, although not necessarily, in the nature of the catalyst depending on whether it is a hydrogen or an oxygen electrode.

The invention will be better understood with reference to the attached drawings, given by way of nonlimiting example. In these drawings, which are all cross sections:

- Figure 1 is a schematic view showing the principle of the fuel cell according to the invention;

- Figure 2 is a detailed view of the interface between the solid film and the porous matrix filled with liquid electrolyte; and

- Figure 3 is an enlarged view of Figure 2, explaining how the cell works.

As Figure 1 shows, where for reasons of clarity the solid film is shown coating the internal face only of the electrode, the cell consists of two electrodes 1 and 2 enclosing porous matrix 3 filled with acidic liquid electrolyte 4. For the liquid electrolyte, it is possible to choose sulfuric acid or phosphoric acids, for example. As far as the matrix is concerned, which must certainly be electrically insulating, it may be made of porous structures of polyethylene or polypropylene mixed with a fine silica powder.

As Figure 2 shows in greater detail, the electrode is composed of conducting substrate 5, which may be chosen from among porous carbons, metal carbides, etc. Substrate 5 has pores 7

extended by channels 6, on the surface of which catalyst 8 is dispersed. Catalyst is also to be found on the internal face of the electrode, in other words, on the face of the electrode that is in contact with porous matrix 3 filled with liquid electrolyte 4.

For catalyst 8, it is possible to use platinum, metal carbides, such as tungsten carbide, for example, for the hydrogen electrode, or dispersed and pyrolyzed metal porphyrins for the oxygen electrode. Finally, coating the whole thing, the internal face of the electrode and channels 6, is solid film 9 consisting of a proton-conducting polymer. For the polymer, it is possible to use one of the above-mentioned substances, such as perfluorinated polymers carrying SO_3- groups such as those sold by Dow Chemical, or by Du Pont de Nemours under the Nafion trademark.

As Figure 3 shows, where the oxygen or positive electrode is illustrated, oxygen gas comes into contact with catalyst 8 by taking channel 6 and passing through film 9. Also arriving at catalyst 8 are hydrogen ions from matrix 3 filled with liquid electrolyte 4 and the electrons supplied by conducting substrate 5. The oxygen reacts with these entities to form water, which is diffused through solid film 9 and eliminated via channels 6.

The hydrogen may be pure or diluted with inert gases, such as N_2 or CO_2, for example., or even an ammonium cracking or alcohol reforming gas, which is rich in H_2. The oxygen may be pure or diluted with inert gases, such as air in particular.

<u>Examples 1 to 6</u>

A triple contact electrode is made by means of a coating operation by laminating-compacting in a gold metallic foam (Examples 1 and 2), or by mechanically coating a substrate of porous carbon made by Stackpole under the brand name Stackpole PC 206 (Examples 3 and 4), or by Zoltek under the brand name Panex PW3 (Examples 5 and 6) with a mixture containing 20 mg/cm^2 of carbon black sold by Cabot under the brand name Vulcan (Examples 1, 3, and 5) or by Degussa under the brand name Printex (Examples 2, 4, and 6), which is lined with a platinum dispersion at a rate of 10 wt% in relation to the carbon, and a binder in the form of a suspension of polytetrafluoroethylene PTFE 30 N, such that the PTFE weight / (carbon weight + Pt weight) = 0.36 before coating-drying the mixture and reworking it with isopropanol for lamination, and then it is dried for 2 h at 300°C. This electrode is vacuum-filled with a solution of Nafion 117 (Du Pont de Nemours trademark distributed by Aldrich) at 5%, so that the weight of the Nafion 117 is between 5 and 10 mg/cm^2.

After drying, the two electrodes so formed are placed in an assembly that plates them onto a matrix of porous polyethylene with a thickness of 0.2 mm, saturated with a 2N solution of H_2SO_4. By supplying one of the electrodes with O_2 and the other with H_2, with suppression of about 50 g/cm^2, we find that at 23°C the system yields current on the order of 200 mA/cm^2 at a voltage of 0.7 V, which value is roughly the same for all Examples 1 to 6.

Claims

1. Fuel cell comprising at least two porous electrodes (1, 2), a catalyst (8) being dispersed on the surface of the pores (7), characterized in that the pores (7) and the inner face of the electrodes (1, 2) are lined with a solid electrolyte in the form of a solid film (9) consisting of a proton-conducting polymer, and that the electrodes (1, 2) enclose, by their internal face, a porous matrix (3) filled with an acidic liquid electrolyte (4).

2. Cell according to Claim 1, characterized in that the capillary tension that holds the liquid electrolyte in the matrix (3) is greater than that between the liquid electrolyte (4) and the pores (7) that constitute the electrodes (1, 2).

3. Cell according to Claim 1 or 2, characterized in that the surface resistance of the matrix (3) filled with liquid electrolyte (4) is less than 0.3 $\Omega \cdot cm$.

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5. Cell according to Claim 1, characterized in that the solid polymer film is an aminosil of the type:

$$(SiO_3)_2 - (CH_2)_3 NH_2, HNX.$$

6. Cell according to Claim 1, characterized in that the solid polymer electrolyte is a perfluorinated compound.

7. Cell according to Claim 1 or 4, characterized in that the thickness of the proton-conducting film (4) [sic] is between 20 and 2000 Å.

8. Cell according to Claim 1, characterized in that the porous substrate (5) on which the catalyst (8) is dispersed and on which the proton-conducting film (7) [sic] is deposited, contains at least one hydrophobic ingredient.

9. Cell according to Claim 8, characterized in that the hydrophobic ingredient is a polytetrafluoroethylene.

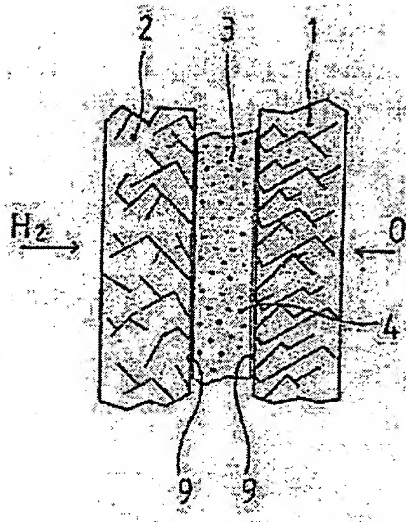

FIG 1

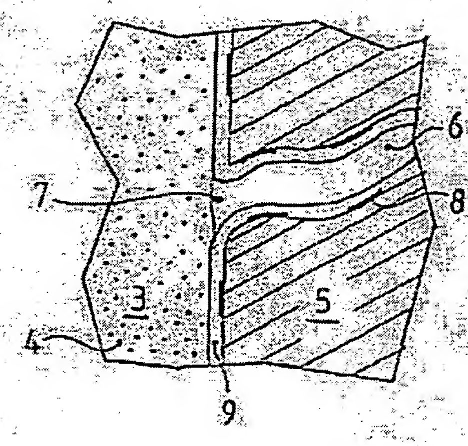

FIG 2

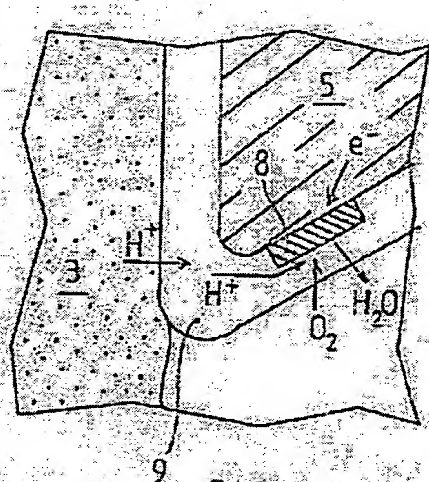

FIG 3

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A	PATENT ABSTRACTS OF JAPAN, vol. 7, No. 239 (E-206) [1384], October 25, 1983; & JP-A-58 128 668 (HITACHI SEISAKUSHO) August 1, 1983 *entire abstract* ---	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 11, No. 187 (E-516) [2634], June 16, 1987; & JP-A-62 017 953 (HITACHI LTD) January 26, 1987 *entire abstract* ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.[5])
A	EXTENDED ABSTRACTS, vol. 86-2, October 19-24, 1986, abstract No. 160, page 237, Princeton, NJ, US; M.N. SZENTIMAY et al.: "Oxygen Reduction at Perfluorosulfonate Ionomer Film-coated Pt Electrodes - Kinetics and Permeability" *Page 237, left column, paragraph 2* ---	1	
A	US-A-3 297 484 (L.W. NIEDRACH) *Claims 1, 11, 12* ---	1	

Date of completion of the search	Examiner
June 25, 1991	J. W. D'Hondt

CATEGORY OF CITED DOCUMENTS

X: Particularly relevant if taken alone.
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A: Technological background.
O: Non-written disclosure.
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T: Theory or principle underlying the invention.
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D: Document cited in the application.
L: Document cited for other reasons.

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FRENCH REPUBLIC
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Application Number

SEARCH REPORT
established on the basis of the most recent claims filed before the start of the search

Fr 9012583
FA 450805

DOCUMENTS CONSIDERED TO BE RELEVANT		Claims concerned in the examined document	
Category	Citation of document with indication where appropriate, of relevant passages		
X	EXTENDED ABSTRACTS, vol. 86-1, May 4-9, 1986, abstract No. 537, Spring Meeting, Boston, MA, US; S. SRINIVASAN et al.: "Enhanced Electrode Kinetics in Phosphoric Acid Fuel Cells by Use of Nafion Coated Porous Gas Diffusion Electrodes" *Page 773, left column, paragraphs 2-3; right column, paragraph 2*	1,4,6	
Y	--- IDEM	2,8,9	
Y	--- US-A-4 610 938 (A.J. APPLEBY) *Claims 1, 4; column 1, lines 56-61; column 2, line 34 – column 3, line 20; example*	8,9	
Y	--- GB-A-2 047 457 (ENERGY RESEARCH CORP.) *Claim 18*	2	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	--- CH-A-510 332 (AG BROWN & BOVERI) *column 3, lines 56-58; Claim 1*	2	H 01 M
X	--- PATENT ABSTRACTS OF JAPAN, vol. 9, No. 75 (E-306) [1798] April 4, 1985; & JP-A-59 209 278 (HITACHI SEISAKUSHO K.K.) November 27, 1984 *entire abstract*	1,4,6	
Y	--- US-A-4 517 260 (K. MITSUDA) *Claim 1; Figure 2a; column 4, lines 3-10* --- -/-	1	

Date of completion of the search	Examiner
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L: Document cited for other reasons.

&: Member of the same patent family, corresponding document.

DERWENT-ACC-NO: 1992-177254
DERWENT-WEEK: 199222

TITLE: Hydrogen-oxygen fuel cell - uses solid electrolyte made of conductive polymer over porous electrodes which enclose porous matrix holding acid electrolyte

INVENTOR: BESSE, S; BRONOEL, G; TASSIN, N

PATENT-ASSIGNEE: SORAPEC SARL [SORAN]

PRIORITY-DATA: 1990FR-0012583 (October 8, 1990)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
FR 2667728 A1	April 10, 1992	N/A	015	H01M 004/86

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
FR 2667728A1	N/A	1990FR-0012583	October 8, 1990

INT-CL (IPC): H01M004/86; H01M008/00
ABSTRACTED-PUB-NO: FR 2667728A

BASIC-ABSTRACT:
The fuel cell has two porous electrodes (1,2) with a catalyser (8) dispersed over the pores (7). The pores and the internal face of the electrodes are coated with a solid electrolyte formed as a solid film (9) of a conductive polymer. The electrodes enclose a porous matrix (3) filled with an acidic liq electrolyte (4).

The capillary tension that retains liq. electrolyte in the matrix is greater than that between the liq. electrolyte and the electrode pores.

ADVANTAGE - Fuel cell without membrane, reducing cost of mfr. and reducing cell internal resistance.

CHOSEN-DRAWING: Dwg.2/3

WO0054351(A1).pdf

CLIPPEDIMAGE= FR002667728A1
PUB-NO: FR002667728A1
DOCUMENT-IDENTIFIER: FR 2667728 A1
TITLE: Fuel cell

PUBN-DATE: April 10, 1992

INVENTOR-INFORMATION:

NAME	COUNTRY
GUY, BRONOEL	N/A
SERGE, BESSE	N/A
NOELLE, TASSIN	N/A

ASSIGNEE-INFORMATION:

NAME	COUNTRY
SORAPEC	FR

APPL-NO: FR09012583
APPL-DATE: October 8, 1990

PRIORITY-DATA: FR09012583A (October 8, 1990)
INT-CL_(IPC): H01M004/86; H01M008/00
EUR-CL (EPC): H01M004/86; H01M008/08

ABSTRACT:
The fuel cell comprises at least two porous electrodes, a catalyst (8) being dispersed on the surface of the pores (7). The pores (7) and the inner face of the electrodes are lined with a solid electrolyte in the form of a film (9) consisting of a proton conduction polymer, and the electrodes enclose, by their internal face, a porous matrix (3) filled with an acidic liquid electrolyte (4).

The solid film (9) of proton conduction polymer, which may be a continuous film, may consist of an aminosil of the type: <IMAGE> or a perfluorinated compound. <IMAGE>